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Introduction to Recombination in Plasmas

by

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Introduction to Recombination in Plasmas

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I - Introduction

The main purpose of these lectures is to review some atomic processes important in recombination. The general recombination problem is extremely broad and complex, and only a few highly idealized situations are considered. Although the choice of material has been governed by the recent renewed interest in recombination, a complete review of the recent developments is not attempted. The emphasis has been placed instead on the quantum and statistical mechanics of the fundamental processes.

As in all non-equilibrium problems, the temporal behavior of a re-combining system depends greatly on the initial state and on the nature of the system under study. For simplicity, we discuss recombination in dilute, monatomic gases which are not in any external fields. Numerical estimates are, in fact, confined to hydrogenic plasma which, of course, has astrophysical interest. By making such drastic limitations at the very start, we obtain a problem which almost is amenable to theoretical treatment.

The processes which occur in such a plasma gas can be divided into two classes, according to whether or not they involve a single hydrogenic system undergoing a one-photon transition. The processes in the simple (purely hydrogenic) class are:

(a) Bound-Bound Transitions: Spontaneous emission
Induced emission and absorption

(b) Bound-Free Transitions: Photoionization
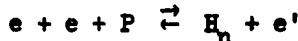Radiative Recombination

(c) Free-Free Transitions

Of course, the ion density must be low enough to consider these processes as occuring for a single electron in the Coulomb field of a free proton. Since we are mainly interested in recombination, we shall not discuss the free-free transitions at all. In addition, we assume that the plasma is transparent to all radiation (and that the radiation is so weak that in-duced emission is unimportant). This means that the only radiative transitions considered are:

Radiative Recombination: $e + P \rightarrow H_n + \hbar\omega$

Spontaneous Emission: $H_n \rightarrow H_{n'} + \hbar\omega_{nn'}$

where the subscript n means the nth bound state.

The most important processes in the second (non-simple) class involve interactions between two or more particles. There are, of course, the very frequent Coulomb collisions between pairs of charged particles. (We shall not discuss these at all, but recognize that they are responsible for the establishment of equilibrium velocity distributions for the free particles.) The most important recombination process in this class involves the collision of two electrons in the field of a proton, leading to a final state in which a bound hydrogen atom is produced and a free electron. Taking into account the inverse process and inelastic scattering, the three-body processes to be considered are three-body recombination and its inverse, electron ionization $\Big\}$ $e + e + P \rightleftarrows H_n + e'$

<u>inelastic</u> and <u>superelastic scattering</u>: $e + H_n \rightleftarrows H_{n'} + e'$

We, therefore, intend to review the role of six processes in re-combination: radiative recombination, spontaneous emission, three-body recombination, and e-H collisions leading to ionization and other bound states. Work on these problems started about 1920, and they have recently attracted much new interest. The early work emphasized the use of de-tailed balance arguments to relate processes and their inverses, and classical theories of radiative and collision processes. This situation has hardly changed with respect to the microscopic processes since the quantum expressions for radiative transitions bring very small corrections, and because no reliable quantum theory for the collision processes exists. A short list of the most important references organized according to sub-ject matter is given at the end of these notes. References to these articles will be made in the notes with a square bracket notation; e.g., [A1] means the standard reference book by Massey and Burhop.

These notes were the basis for a series of four lectures given in the Atomic Physics Seminar at Berkeley during the fall semster of 1962. They contain essentially no original material and are intended to serve the beginning student of recombination problems. The material is divided into roughly three parts, dealing with radiative recombination, three-body re-combination, and a short description of the physical processes in a moderately dense plasma. Most emphasis has been placed on Section III on three-body recombination.

II - Photoionization and Recombination

A. Photoionization Cross Section

We begin with the absorption cross section for hydrogenic atoms

$$\sigma_n(Z, \hbar\omega) = \frac{64}{3\sqrt{3}} \alpha \pi a_o^2 \frac{n}{Z^2} \left(\frac{I_n}{\hbar\omega} \right)^3 g_n(u) \, ,$$

using familiar notation except perhaps for the Gaunt factor, g_n. The ejected electron energy is

$$E = \hbar\omega - I_n \qquad\qquad I_n = \left(\frac{Z^2}{n^2} \right) R$$

and

$$u = \frac{E}{I_n}$$

where R is the ionization energy for H in its ground state. The above expression with unit Gaunt factor was derived classically by Kramers in 1923 [B1], i.e., before quantum mechanics. The wave mechanical calculation of Gaunt [B2] simply led to the extra factor, $g_n(u)$, which tends to one for large n and small u, i.e., in the classical limit. For example, not more than a 20% error is incurred (for the average g_n appearing here) for $u < 1$, although the deviation for particular subshells can be larger. If necessary, an asymptotic series or extensive tabulations may be used to improve on the simple Kramers formula (Burgess, Menzel and Pekeris [A4], and Karzus and Latter. See [A3] for references to this work.)

At threshold, the cross section for photoionization of H in its ground state is simply

$$\sigma_1(1, R) = \frac{64}{3\sqrt{3}} \alpha \pi a_o^2 = 8 \times 10^{-18} \text{ cm}^2 \, .$$

This value is larger by 10 than the obvious order of magnitude, $\alpha \pi a_o^2$, because of the various numerical factors.

For hydrogen, the photoionization cross section is, at
least in principle, known exactly in terms of the hypergeometric
wave functions. For heavier atoms and ions, except perhaps for
Be, the situation is not anywhere as good. This is particularly
true for the energies involved in most recombination problems,
i.e., energies rather small than a Rydberg, where good atomic
wave functions for both initial and final states are important.
The situation has been so poor that systematic studies of the
photoionization cross section in the Hartree approximation have
only recently been published (for rare gas atoms, see J. W. Cooper,
Phys. Rev. $\underline{128}$, 681). Also, the first work on correlation effects
in the atomic photoeffect has just been finished by Dr. Phillip
Altick and the writer (to be published). The usual practice
in the past has, of course, been to make some kind of hydrogenic
approximation.

If we have a density of atoms, n_r, in the rth level and a
directed photon beam with an energy density, $I(\hbar\omega)d(\hbar\omega)$ in the
interval, $d(\hbar\omega)$, then the rate of decrease in n_r due to
photoionization is

$$\left(\frac{dn_r}{dt}\right)_{photoion} = - n_r \int_{I_r}^{\infty} d(\hbar\omega) \; \frac{c}{4\pi} I(\omega) \frac{1}{\hbar\omega} \; \sigma_{ion}^{(r)} (Z,\hbar\omega)$$

This defines a photoionization time, τ_r

$$\frac{1}{\tau_r} = \int_{I_r}^{\infty} d(\hbar\omega) \frac{c}{4\pi} I(\omega) \frac{1}{\hbar\omega} \sigma_r(Z,\hbar\omega) \; ,$$

which will appear in rate equations or will be useful in making rough estimates. In many problems, the radiation can be represented by a Planck distribution with an effective temperature, T_o, and a reduction factor, λ, (arising from absorption)

$$I = \lambda \, 8 \, \pi \left(\frac{\nu}{c}\right)^3 f\left(\frac{\hbar\omega}{kT_o}\right) \; ,$$

where

$$f\left(\frac{\hbar\omega}{kT_o}\right) = \frac{1}{e^{\hbar\omega/kT_o} - 1}$$

Furthermore, the radiation density may be very weak in the spectral region of interest, i. e., $I_r \gg kT_o$

$$f \approx e^{-\hbar\omega/kT_o} \ll 1 \; .$$

These assumptions lead to a photoionization frequency

$$\frac{1}{\tau_r} = \left(\frac{2}{3\sqrt{3}\pi^2}\right) \alpha^4 \left(\frac{c}{a_o}\right) \frac{Z^4}{r^5} \lambda E_1\left(\frac{I_r}{kT_o}\right) \, ,$$

where we should really put in the asymptotic value of the exponential integral: $E_1(a) \rightarrow e^{-a}/a$. Thus we obtain a useful approximate formula

$$\frac{1}{\tau_1} \approx 6 \times 10^8 \text{ sec}^{-1} \lambda \frac{e^{-I_r/kT_0}}{I_r/kT_0} \left(\frac{Z^4}{r^5}\right) \ .$$

Because $I_r/kT_0 \gg 1$, the photoionization time is considerably longer than typical fast radiative lifetimes of the order of 10^{-8} sec.

B. Radiative Recombination Cross Section

Radiative recombination of an electron and a proton, for example, is just the inverse of the photoionization of the hydrogen atom. If we know the cross section for one process, we can obtain the inverse by detailed balancing, as was first done by Milne in 1924.

The photoionization cross section discussed above refers to the total number of electrons with energy

$$E(k) = I_r - \hbar\omega \ ,$$

(integrated over their directions) ejected by unpolarized photons of energy, $\hbar\omega$, incident on unpolarized H atoms in the rth level, all per unit photon flux and for one atom. In first order perturbation theory, the cross section is

$$\sigma_{ion}^{(r)} (\hbar\omega) = \frac{1}{2} \sum_{\hat{e}} \frac{1}{2} \sum_{r} \sum_{\ell m} \frac{2\pi}{\hbar} |(\vec{k}|H'|n\ell m, \hat{e})|^2 \frac{4\pi k^2 dkV}{(2\pi)^3 dE} \left(\frac{c}{V}\right)^{-1}$$

In addition to the standard Golden Rule formula consisting of $\frac{2\pi}{\hbar}$ x square of matrix element x density of states, this expression has been divided by the photon current, and averaged over photon and atom polarizations.

We think of the inverse process as a beam of electrons of energy, $E(k)$ interacting with a (stationary) gas of protons leaving H atoms in the rth level with the emission of photons with energy

$$\hbar\omega = I_r + E(k) \ .$$

Once again the total cross section is calculated, in that a sum is carried out over photon directions and polarizations and over the sub-states of the atomic level. The first-order perturbation theory

expression is now

$$\sigma_{rec}^{(r)} (\hbar\omega) = \sum_{\ell_m} \sum_{\mathcal{E}} \frac{2\pi}{\hbar} |(n\ell_m \, \mathcal{E}|H'|k)|^2 \frac{4\pi\kappa^2 d\kappa V}{(2\pi)^2 d(\hbar\omega)} \left(\frac{v}{V}\right)^{-1}$$

Taking advantage of the Hermitian nature of H', we form the ratio of the cross sections

$$\frac{\sigma_{rec}^{(r)} (E)}{\sigma_{ion}^{(r)} (\hbar\omega)} = \frac{\kappa^2 \frac{d\kappa}{d(\hbar\omega)} \frac{1}{v}}{k^2 \frac{dk}{dE} \frac{1}{c} \left(\frac{1}{2r^2}\right)}$$

Now $dE/d(\hbar\omega) = 1$ and $\frac{\hbar^2}{m} kdk = c\hbar d\kappa$, so that

$$\frac{\sigma_{rec}^{(r)}}{\sigma_{ion}^{(r)}} = r^2 \frac{\kappa^2}{k^2} \, 2 \left(\frac{d\kappa}{dk}\right)\left(\frac{c}{v}\right)$$

$$= r^2 \frac{\kappa^2}{k^2} \, 2 \left(\frac{\hbar k}{mc}\right)\left(\frac{c}{v}\right)$$

or (Milne's formula)[B2]

$$\frac{\sigma_{rec}}{\sigma_{ion}} = 2r^2 \frac{\kappa^2}{k^2} = r^2 \frac{(\hbar\omega)^2}{mc^2 E(k)} \quad .$$

Before taking advantage of this result of "detailed balancing," we should immediately note two of its obvious consequences. First of all, the recombination cross section becomes very large as the electron energy approaches zero. (Of course, this means the emitted photon's energy approaches the ionization potential, I_r, in this limit.)

[†]This elementary derivation is somewhat redundant in that an improved and more general discussion of detailed balancing for two-body reactions is given in Section III-A.

Since σ_{ion} is finite at threshold, the recombination cross section
has the limiting form

$$\sigma_{rec} \underset{E \ll I_r}{\rightarrow} \sigma_{ion} \, r^2 \, \frac{I_r^2}{(mc^2) \, E}$$

On the other hand, one must be very close to zero energy since the ratio
involves the rest energy, mc^2, in the denominator. In particular, the
energy must be less than $(I_r/mc^2) \, I_r$ before σ_{rec} becomes larger than
σ_{ion}. For $Z = 1$ and $r = 1$, this means an energy of less than 4×10^{-4} eV.
More typically, we might quote the recombination cross sections to the
ground state of the H-atom at 2×10^{-2} eV and 1 eV:

$$\sigma^{(1)} \, (1, \, 2 \times 10^{-2} \text{ eV}) \; \widetilde{=} \; 4 \times 10^{-20} \text{ cm}^2$$

$$\sigma^{(1)} \, (1, \, 1 \text{ eV}) \; \widetilde{=} \; 2 \times 10^{-22} \text{ cm}^2 \; .$$

The actual recombination cross section, obtained from the previous
ionization cross section with the detailed balance result, is

$$\sigma_{rec}^{(r)} \, (Z, E) \; = \left(\frac{32}{3\sqrt{3}} \, \alpha^3 \, \pi \, a_o^2 \right) r \; \frac{1}{u(1 + u)} \; g_r(u) \; ,$$

where $u = E/I_r$, $g_r(u)$ is the bound-free Gaunt factor and the coefficient
is

$$\frac{32}{3\sqrt{3}} \, \alpha^3 \, \pi \, a_o^2 \; = \; 2.13 \times 10^{-22} \text{ cm}^2 \; = \; 2\sigma^{(1)}(u = 1) \; .$$

We note that the ionization cross section is of the order $\pi \, a_o \, \lambda_c$,
whereas the recombination cross section is of order $\pi \, \lambda_c \, r_o$ (λ_c and r_o
being the Compton and classical electron radii).

We are often interested in the rate at which electrons recombine to form
atoms in the various atomic energy levels. Because of the large number
of particle-particle collisions, it is usually possible to assume that
the electrons and ions are in thermal equilibrium. Unless the effective
ion temperature is very much greater than the effective electron temp-
erature, the relative velocity is mainly due to the electrons because
of their smaller mass. Representing the electron velocity distribution

with a Maxwell distribution with an electron temperature, T_e, the number per unit volume with speeds in the range v to v + dv is

$$f(v)dv = n_e \left(\frac{m}{2\pi kT_e}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT_e} 4\pi v^2 dv$$

where n_e is the electron density. Then the number of recombinations per unit volume in which electrons in dv recombine with protons to form "H atoms" in the level r is

$$n_i f(v)dv \, v \, \sigma_{rec}^{(r)}(Z,E) \ .$$

In terms of the energy distribution, $g(E)dE = f(v)dv$

$$g(E)dE = n_e \frac{2}{\sqrt{\pi}} e^{-E/kT_e} \frac{\sqrt{E}dE}{(kT_e)^{3/2}} \ ,$$

and the above recombination cross section, this rate is   (take $g_r(u) = 1$)

$$n_i n_e \frac{2}{\sqrt{\pi}} \frac{e^{-E/kT_e}\sqrt{E}dE}{(kT_e)^{3/2}} \sqrt{\frac{2E}{m}} 2\sigma_{rec}^{(1)}(u=1) \ \frac{1}{\frac{E}{I_r}\left(1+\frac{E}{I_r}\right)}$$

where $\sigma^{(1)}(u=1) \approx 10^{-22} \ cm^{-2}$. Integrating over all energies, E, and introducing the mean electronic speed

$$\bar{v} = \sqrt{\frac{8kT}{m\pi}}$$

we obtain the total radiative recombination rate into the level, r,

$$\left(\frac{dn_r}{dt}\right)_{rec} = \alpha_r n_i n_e \ ,$$

where the recombination coefficient, α_r, is

$$\alpha_r = \bar{v} \, \sigma_{rec}^{(1)}(1) \, 2r\left(\frac{I_r}{kT_e}\right)^2 e^{I_r/kT_e} E_1\left(\frac{I_r}{kT_e}\right) \ .$$

This formula gives the rate of direct radiative recombination of electrons and protons into the rth level. We can examine its value in

two limits, $I_r \ll kT_e$ and $I_r \gg kT_e$, using the well-known behavior of the exponential integral.

$$E_1(x) \rightarrow \begin{cases} e^{-x}/x & x \rightarrow \infty \\ -\ln \gamma x & x \rightarrow 0 \end{cases}$$

$\ln \gamma = 0.5772$ (Euler-Mascheroni constant). Thus, if we consider a particular level, r, the direct recombination varies for low temperatures as

$$\alpha_r \underset{kT_e \ll I_r}{\rightarrow} [\bar{v} \, \sigma_{rec}^{(1)} (1)] \, 2r \left(\frac{I_r}{kT_e} \right) .$$

Because $\bar{v} \propto T_e^{1/2}$, α_r is inversely proportional to the square root of the temperature. This is understandable from the 1/E threshold behavior for radiative capture and the $\sqrt{E}$ dependence of the relative velocity. As an example, consider recombination to the ground state of H at 1200°K, for which the following numerical estimates hold:

$$\bar{v} \approx 2 \times 10^7 \text{ cm/sec}$$
$$\bar{v} \, \sigma_{rec}^{(1)} (1) \approx 2 \times 10^{-15} \text{ cm/sec}$$
$$\alpha_1 \approx 6 \times 10^{-13} \text{ cm/sec}$$

In this limit, we observe that $\alpha_{rec}^{(2)} \propto \frac{1}{r}$.

The dependence of α_r on r and T_e can be understood in terms of the function

$$G_1(x) = xe^{xE_1(x)} ,$$

which has the properties in the interval, $0 \le x \le \infty$: $G(0) = 0$, $G(\infty) = 1$, $G'(x) \ge 0$. Thus, for fixed r, the cross section is a decreasing function of T_e, going like $T_e^{1/2}$ for small T_e and $T_e^{3/2} \log T_e$ for large T_e. For fixed T_e, it decreases with principal quantum number varying like 1/r if $I_r \gg kT_e$. The latter dependence is not particularly strong so that the higher states are appreciably populated by recombination. The discrete lines which result give use to the recombination lines seen in spectroscopic work.

C. Discussion of Radiative Recombination

We have discussed in some detail the "total" recombination to a particular hydrogenic level. We could go on along these lines and discuss, for example, recombination with complex ions, how the recombination rate, α_r, is broken down into partial rates

$$\alpha_r = \sum_\ell \alpha_{r\ell} \, ,$$

and corrections due to the Gaunt factor. Very briefly, the theoretical situation for complex ions is very poor because of the extreme difficulty in obtaining good wave functions for both initial and final states. At the present time, one is restricted to using hydrogenic approximations for recombination to excited levels and hoping for measurements of the photoionization cross section in the ground state. The variation of $\alpha_{n\ell}$ with ℓ is quite significant and for H depends on n and T_e. For large n, there is a maximum near $\ell = \frac{1}{3}$ n (empirical rule). Finally, the role of the Gaunt factor has been exhaustively studied by Seaton who has been interested in obtaining radiative recombination coefficients to much better than 20% [B3 and A3].

Of somewhat more interest here is the role of these recombination coefficients in determining the distribution of electrons and atomic energy levels in a plasma. As mentioned previously, this is an extremely complicated problem which is very sensitive to the particular system under consideration. The simplest situation is a dilute plasma, by which we mean one transparent to radiation. In other words, the statistical distribution of the radiation field is excluded from consideration. (One could be a little more general by allowing the medium to absorb one or more particular frequencies.)

The only role of radiation in a dilute plasma is an energy loss mechanism. The radiation will be of three kinds according to the three radiative loss processes

$$\left\{ \begin{array}{ll} \text{free-free} & \text{(Bremstrahlung)} \\ \text{free-bound} & \text{(Recombination Radiation)} \\ \text{bound-bound} & \text{(Spontaneous Decay)} \end{array} \right.$$

We shall not discuss the free-free transitions, which, of course play a role in determining the electron temperature. In discussing the rate at which the population, n_r of the rth level, changes, the recombination

process gives, of course, the direct contribution, $\alpha_r n_i n_e$. But the spontaneous decay of all the levels is important, too, since the level, r, will be depleted by transitions to lower levels and populated by transitions from higher levels:

$$\frac{dn_r}{dt} = \alpha_r n_i n_e + \sum_{s>r} A(s,r) m_s - \sum_{g<r} A(r,g) m_r .$$

The total rate of change in the density of atoms, $n = \sum_r n_r$, must be equal to the negative of the rate of change of electrons,

$$\frac{dn_e}{dt} = - \frac{dn}{dt} = - \sum_r \frac{dn_r}{dt}$$

On substituting the above expressions for dn_r/dt, the terms involving bound-bound transitions cancel so that

$$\frac{dn_e}{dt} = - \alpha n_i n_e ,$$

where the total recombination coefficient is

$$\alpha = \sum_{r=1}^{r_m} \alpha_r .$$

This quantity is of interest since it determines the decay of the electric charge density, a quantity which can be measured experimentally. To obtain the actual populations, we must, of course, solve this infinite set of coupled equations. The simplest situation is the equilibrium one; every $dn_r/dt = 0$. This is often of practical interest even if $dn_r/dt \neq 0$, since it may be smaller than all the terms on the right side of the equation This limit is also often of interest in astrophysical problems. For a hydrogen plasma, Seaton has obtained the most accurate solution of the equilibrium distribution. Rather good agreement can be obtained in this way with observations on planetary nebulae. It must always be remembered that the present discussion completely ignores particle-particle collisions (which, of course, are important in determining temperatures) and also the details of the recombination for dense plasmas.

Finally, we summarize the properties of the total radiative re-
combination coefficient. The upper limit to the summation is determined
by the particle density, since arbitrarily large Bohr orbits are readily
destroyed by collisions. Unlike the partition sum, the series converges,
so that for an infinitely dilute plasma the recombination coefficient has
a well-defined value. Numerical values as a function of temperature are
as follows:

T ($^{\circ}$K)	α
250	4.84×10^{-12} cm^3/sec
500	3.12
1,000	1.99
2,000	1.26
4,000	7.05×10^{-13}
8,000	4.83
16,000	2.93
32,000	1.73
64,000	1.00

The temperature variation is roughly as $T^{-0.7}$. If we compare
$\alpha_1 = 5 \times 10^{-13}$ cm^3/sec at 1000°K with the total, $\alpha = 2 \times 10^{-12}$, we
see that $\alpha_1 \approx \frac{1}{4} \alpha$; i.e., recombination to higher states and their radiative
decay to lower ones is important in obtaining the correct value of the
total α.

Seaton has also studied the rate at which electron kinetic energy is
lost by recombination in terms of the coefficients, β_r,

$$\frac{dU_r}{dt} = - \beta_r kT \, n_i n_e \; .$$

He finds that the total rate, $\beta = \sum_r \beta_r$, is roughly $\frac{\alpha}{6}$.

## III - The Microscopic Three-Body Recombination Process

Unlike the situation for radiative recombination, the microscopic
theory for three-body recombination and its inverse, ionization by
electron bombardment, is not well understood. For this reason, we begin
the discussion with what is completely general and exact, the application
of detailed balance and microscopic reversibility to these processes.
Once more, the scant experimental and theoretical information is on the
ionization cross section, not the recombination process of direct interest
here. At the same time, we will briefly discuss the inverse processes
of inelastic and superelastic collisions, the so-called collisions of
the first or second kind, which are closely related to and essential for
studying recombination.

A. Microscopic Reversibility and Detailed Balance for Inelastic and
    Superelastic Collisions

In 1921, Klein and Rosseland first deduced the existence of super-
elastic collisions, in which an electron gains energy by collision with
an excited atom, from the Principle of Detailed Balancing [Cl]. They
argued that an ionized gas could only be in equilibrium if the rate at
which atoms were excited by electron collisions from state n to n to n'

$$e + H_n \rightarrow e' + H_{n'}$$
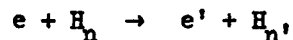
was equal to the rate at which they were de-excited by the inverse process

$$e' + H_{n'} \rightarrow e + H .$$
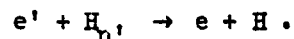
A few years later, Kramers and Milne applied a similar argument to the
photodisintegration and radiative capture problem, as we have already
discussed in detail. These kinds of arguments go back to Einstein's
famous discussion of the equilibrium between the radiation field and a
system of bound atoms, which led him to discover induced emission and to
introduce the A and B coefficients. The Kramers-Milne discussion may,
in fact, be considered as an extension of Einstein's work to radiation
equilibrium with material systems which are ionized.

We shall now re-derive the Klein-Rosseland result from the more
general Principle of Microscopic Reversibility. In other words, we
will obtain our detailed balancing from the invariance principles of

the quantum mechanical equations of motion. Before the advent of the quantum theory, the principle of detailed balancing was derived as the sufficient, but not necessary, condition for the preservation of thermal equilibrium, as we discuss in some detail below.

We consider first the general reaction in which two systems in levels 1 and 2 approach with relative velocity, v, and recede in levels 1' and 2' with relative velocity, v', viewed from the center-of-mass system. For each system, there are g states α with the same energy (e.g., g_1 states α_1 and g_2 states α_2 for the initial state). We assume that the experimental preparation and detection does not distinguish any of these states. The total cross sections for the process $1 + 2 \rightarrow 1' + 2'$ and its inverse $1' + 2' \rightarrow 1 + 2$ are

$$\sigma(1+2 \rightarrow 1'+2') = \int d(\hat{v}') \frac{1}{g_1 g_2} \sum_{\alpha_1 \alpha_2} \sum_{\alpha_1', \alpha_2'} \frac{2\pi}{\hbar} \left| (1'2'|A|12) \right|^2 \frac{k'^2 dk' v}{(2\pi)^3 dE'} \left(\frac{v}{V} \right)^{-1}$$

$$\sigma(1'+2' \rightarrow 1+2) = \int d(\hat{v}) \frac{1}{g_1' g_2'} \sum_{\alpha_1', \alpha_2'} \sum_{\alpha_1 \alpha_2} \frac{2\pi}{\hbar} \left| (12|A|1'2') \right|^2 \frac{k^2 dk V}{(2\pi)^3 dE} \left(\frac{v'}{V} \right)^{-1}$$

The quantities $(1'2'|A|12)$ and $(12|A|1'2')$ are the exact amplitudes for the process, and the last factors are the appropriate density of states divided by the incident current for box normalization of the relative motion. In general, we <u>cannot</u> say that the two amplitudes are equal, but only that time-reversed amplitudes are the same. Now time reversal involves revising spins and momenta but, using rotation and parity invariance, we can show that the <u>average</u> amplitudes are the same, i.e.,

$$\int d(v') \sum_{\alpha_1 \alpha_2 \alpha_1', \alpha_2'} |(1'2'|A|12)|^2 = \int d(\hat{v}) \sum_{\alpha_1 \alpha_2 \alpha_1', \alpha_2'} |(12|A|1'2')|^2$$

therefore

$$\frac{\sigma(1+2 \rightarrow 1'+2')}{\sigma(1'+2' \rightarrow 1+2)} = \frac{g_1' g_2'}{g_1 g_2} \left(\frac{v'}{v} \right) \frac{k'^2 \left(\frac{dk'}{dE'} \right)}{k^2 \left(\frac{dk}{dE} \right)}$$

Recognizing that $(1/v)(dE/dk) = 1$ for both particles and radiation, we arrive at the result of detailed balancing

$$g_1 g_2 k^2 \sigma(1+2 \rightarrow 1'+2') = g_1, g_2, k'^2 \sigma(1'+2' \rightarrow 1+2) \ .$$

We have already used this result for photoionization and radiative recombination (photon energy $\mathcal{E}(k) = c\hbar k$ and electron energy $E(k') = \hbar^2 k'^2/2m$) in Section II-A. For inelastic and superelastic electron scattering from hydrogenic levels: $g_1 = 2 = g_1'$, $g_2 = 2n^2$ $g_2' = 2n'^2$; $E(k) = \hbar^2 k^2/2m$, $E(k') = \hbar^2 k'^2/2m$, and thus the Klein-Rosseland result is obtained.

$$n^2 E \sigma(nE \rightarrow n'E') = n'^2 E' \ \sigma \ (n'E' \rightarrow nE) \ .$$

Next, let us consider the rate at which either one of the levels is changed by the two inverse processes.

$$\left(\frac{dn_r}{dt}\right)_{r \rightarrow r'} + \left(\frac{dn_r}{dt}\right)_{r' \rightarrow r} = - \int_{I_{rr'}}^{\infty} dE g(E) n_r \sqrt{\frac{2E}{m}} \ \sigma(rE \rightarrow r'E')$$

$$+ \int_{0}^{\infty} dE' g(E') n_r \sqrt{\frac{2E'}{m}} \sigma(r'E' \rightarrow rE) \ .$$

Here $g(E)dE$ is the electron density in the energy interval dE, which we assume to be given by the equilibrium Maxwell distribution

$$g(E)dE = n_e \frac{2}{\sqrt{\pi}} e^{-E/kT} \frac{\sqrt{E} \ dE}{(kT)^{3/2}} \ .$$

The quantity $I_{rr'}$ is the difference in ionization potentials, which which arises in the equation expressing energy conservation

$$E - I_r = E' - I_{r'}$$

or

$$E = E' + I_{rr'} \qquad I_{rr'} = I_r - I_{r'}$$

Introducing this equilibrium distribution gives the rate

$$\left(\frac{dn_r}{dt}\right)_{r \to r'} + \left(\frac{dn_r}{dt}\right)_{r' \to r} = \sqrt{\frac{2}{m}} \frac{2/\sqrt{\pi} m_e}{(kT)^{3/2}} \left\{ -\int_{I_{rr'}}^{\infty} dE\, e^{-E/kT} E\sigma(rE \to r'E')n_r \right.$$

$$\left. -\int_{0}^{\infty} dE'\, e^{-E'/kT} E'\sigma(r'E' \to rE)n_{r'} \right\}$$

Incorporating the result of detailed balancing, and changing the variable of integration in the first integral to E' leads to

$$\left(\frac{dn_r}{dt}\right)_{r \to r'} + \left(\frac{dn_r}{dt}\right)_{r' \to r} = \sqrt{\frac{2}{m}} \frac{(2/\sqrt{\pi})n_e}{(kT)^{3/2}} \int_{0}^{\infty} dE'\, e^{-E'/kT} E'\sigma(r'E' \to rE)$$

$$\times \left\{ \frac{r'^2}{r^2} e^{-I_{rr'}/kT} n_r - n_{r'} \right\} .$$

The necessary and sufficient condition for this rate to vanish is

$$\frac{n_{r'}}{n_r} = \frac{r'^2 e^{I_{r'}/kT}}{r^2 e^{I_r/kT}} = \frac{g_{r'} e^{-E_{r'}/kT}}{g_r e^{-E_r/kT}} ,$$

i.e., the equilibrium Maxwell-Boltzmann distribution. The Klein-Rosseland method proceeds the other way round; i.e., starts with atoms and electrons in Maxwell-Boltzmann distributions with the same temperature, and obtains the detailed balance relation between cross sections by requiring preservation of this equilibrium. This method is typical of the way detailed balancing was invoked before quantum mechanics. It should be mentioned that, if more than two levels are considered, this method leads to a somewhat weaker result than the general one.

B. Detailed Balancing and Three-Body Recombination

We now extend these ideas to the inverse processes of three-body recombination and electron disintegration of atoms. Again we start with the quantum mechanical microscopic reversibility and achieve a result obtained by R. H. Fowler in 1924 as the sufficient condition for maintaining the thermal equilibrium of an ionized gas [Cl].

For single ionization processes, we have an unpolarized electron beam with momentum $\vec{k}_0$ incident on atoms in the rth level with statistical weight g_r, producing electrons with momenta $\vec{k}_1$ and $\vec{k}_2$ and an ion in the sth level with statistical weight g_s. The cross section for producing an electron in the solid angle $d(\hat{k}_1)$ and another in the momentum space element $d(\vec{k}_2)$ is

$$\sigma_{ion} (\hat{k}_0 r \to \hat{k}_1 \vec{k}_2 s) \, d (\hat{k}_1) \, d (\vec{k}_2)$$

$$= \frac{1}{g_r} \sum_{\alpha_r} \sum_{\beta_s} \frac{2\pi}{\hbar} |(\vec{k}_1 \vec{k}_2 \beta_s |A| \vec{k}_0 \alpha_s)|^2 \frac{k_1^{\,2} dk_1 d(\hat{k}_1) V}{(2\pi)^3 dE(k_1)} \frac{d(\vec{k}_2) V}{(2\pi)^3} \frac{V}{V_0}$$

The energy of the electron with momentum $\vec{k}_1$ is, of course, determined by energy conservation

$$E(k_0) - I_r = E(k_1) + E(k_2) - I_s \quad .$$

We ignore spin completely and average and sum over the states of the atomic and ionic levels, respectively. Noting that $dE/d(k^2) = \hbar^2/2m$, this reduces to

$$\sigma_{ion}(\vec{k}_0 r \to \hat{k}_1 \hat{k}_2 E_2 s) d(\hat{k}_1) d(\hat{k}_2) dE_2$$

$$= \frac{1}{8} \frac{V^3 \left(\frac{2m}{\hbar^2}\right)^3}{(2\pi)^5} \frac{1}{g_r} \sum_{\alpha_r} \sum_{\beta_s} |(\vec{k}_1 \vec{k}_2 \beta_s |A| \vec{k}_0 r)|^2 \left(\frac{k_1 k_2}{k_0}\right) d(\hat{k}_1) d(\hat{k}_2) dE_2$$

The <u>total</u> cross section for ionization by a beam of electrons with energy E_0 and the production of one electron with energy E_1 and another in the energy range dE_2 is

$$\sigma_{\text{e-ion}}(E_0 r \to E_1 E_2 s) \, dE_2$$

$$= \frac{1}{8} \left(\frac{k_1 k_2}{k_0} \right) \frac{V^3 \left(\frac{2m}{\hbar^2} \right)^{\frac{-2}{?}}}{(2\pi)^5} \int d(\hat{k}_1) \int d(\hat{k}_2) \frac{1}{g_r} \sum_{\alpha_r} \sum_{\beta_s} |(\vec{k}_1 \vec{k}_2 \beta_s |A| \vec{k}_0 \alpha_r)|^2 \, dE_2$$

Next we turn to the three-body recombination process. Because the initial state involves three bodies, the concept of a collision cross-section area is not applicable, and we will be content with the total transition rate.

$$W_{\text{3-rec}}(E_1 E_2 s \to E_0 r) = \int d(\hat{k}_0) \frac{1}{4\pi} \int d(\hat{k}_1) \frac{1}{4\pi} \int d(\hat{k}_2) \frac{1}{g_s} \sum_{\beta_s} \sum_{\alpha_r}$$

$$\times \frac{2\pi}{\hbar} |(\vec{k}_0 \alpha_r |A| \vec{k}_1 \vec{k}_2 \beta_s)|^2 \frac{k_0^2 dk_0 V}{(2\pi)^3 dE(k_0)}$$

In addition to averaging over initial ionic states β_s and summing over final atomic states α_r, we have averaged over all initial electron directions and integrated over all final electron directions. Since the electrons are normalized to unity (in a box), this is the transition probability per unit time that two electrons with energies E_1 and E_2 and an ion in level s will become an atom in level r and a free electron with energy E_0. We might simplify this expression somewhat, taking advantage of the fact that, after integrating over $\hat{k}_1$, $\hat{k}_2$, the expression is independent of $\hat{k}_0$

$$W_{\text{3-rec}}(E_1 E_2 s \to E_0 r) = \frac{1}{4(2\pi)^3} V \left(\frac{2m}{\hbar^2} \right) \frac{k_0}{\hbar}$$

$$\times \int d(\hat{k}_2) \int d(\hat{k}_1) \frac{1}{g_s} \sum_{\alpha_r} \sum_{\beta_s} |(\vec{k}_0 \alpha_r |A| \vec{k}_1 \vec{k}_2 \beta_s)|^2$$

The average matrix elements which appear in $\sigma_{\text{e-ion}}$ and $W_{\text{3-rec}}$ are equal even though the original amplitudes are not (since they refer to inverse rather than time-reversed states). Thus the two results can be combined to give

$$\frac{\sigma_{e\text{-ion}}(E_o r \to E_1 E_2 s)}{W_{3\text{-rec}}(E_1 E_2 s \to E_o r)} = \frac{\frac{1}{8} \frac{\frac{1}{k_2}}{k_o} \frac{v^3 \left(\frac{2m}{\hbar^2}\right)^3}{(2\pi)^5} \frac{1}{g_r}}{\frac{1}{4} \frac{k_o}{\hbar} \frac{\left(\frac{2m}{\hbar^2}\right)}{(2\pi)^3} \frac{1}{g_s}} = \frac{g_s}{g_r} \frac{v^2 \left(\frac{2m}{\hbar^2}\right)^2}{2(2\pi)^2} \hbar \frac{k_1 k_2}{k_o^2}$$

which now leads to the major result of detailed balancing for these processes

$$g_r k_o^2 \sigma(E_o r \to E_1 E_2 s) = g_s k_1 k_2 \left[\frac{v^2 \left(\frac{2m}{\hbar^2}\right)^2}{2(2\pi)^2} \hbar \, W_{3\text{-rec}}(E_1 E_2 s \to E_o r) \right]$$

We check the dimensions of this relation by noting that $v^2(2m/\hbar^2)^2$ has the dimensions of L^2/E^2; whereas $W_{3\text{-rec}}$ has the dimensions of E; hence, σ has the dimensions L^2/E --which is correct.

The appearance of v^2 in this expression may seem a little surprising, but the fact is that $v^2 W_{3\text{-rec}}$ is the quantity which enters into the rate of recombinations. To calculate the rate at which the number of atoms in the rth level changes through this process, we have to multiply $W_{3\text{-rec}}$ by the number of ions and by the number of electrons in two energy intervals: using $g(E)dE$ as the density (number per cm^3) of electrons with energy dE, the number of recombinations into r from s by electrons in dE_1 and dE_2 is

$$W_{3\text{-rec}}(E_1 E_2 s \to E_o r) \, Vn_s \, Vg(E_1)dE_1 \, Vg(E_2)dE_2 \quad ,$$

where n_s is the density of ions in the sth level. Hence the rate at which the density of atoms in level r changes by recombination is

$$\frac{2}{\hbar} \left[\frac{(2\pi)^2}{\left(\frac{2m}{\hbar^2}\right)^2} \right] \frac{g_r}{g_s} \frac{k_o^2}{k_1 k_2} \, \sigma(E_o r \to E_1 E_2 s) \qquad n_s g(E_1)dE_1 g(E_2)dE_2$$

Apparently this elementary derivation of detailed balancing does not appear in the literature. Since the results and notation of Fowler [C1] are very widely used, we now make connections with his results. Fowler introduces the same ionization cross section, but calls it

$S_r^s(E_2, E_0)$(Eq (19) of his 1924 article)

$$\sigma(E_0 r \rightarrow E_1 E_2 s) = S_r^s(E_2, E_0) \ .$$

(Our use of the energy E_1 is, of course, redundant since it is determined by energy conservation.) Next Fowler writes the above recombination rate as [his Eq(22)]

$$n_s \sqrt{\frac{2E_1}{m}} \ g(E_1)dE_1 \ \sqrt{\frac{2E_2}{m}} \ g(E_2)dE_2 \ S_s^r(E_1, E_2) \ .$$

We see that he introduces velocity factors in analogy to two-body processes where a cross section would be appropriate. (The entity S_s^r has the dimensions $L^4 T$.) In any case, we can make the identification

$$S_s^r(E_1, E_2) = \frac{v^2}{v_1 v_2} \ W_{3-rec}(E_1 E_2 s \rightarrow E_0, r) \ .$$

We can finally substitute these new quantities (Fowler's) into our detailed-balancing result to obtain

$$g_r k_0^2 \ S_r^s(E_2, E_0) = g_s k_1 k_2 \ v_1 v_2 \ \frac{\left(\frac{2m}{\hbar^2}\right)^2}{2(2\pi)^2} \ \hbar \ S_s^r(E_1 E_2)$$

Multiplying through by $\hbar^2/2m$ and remembering that $vp = 2E$, this becomes

$$g_r E_0 S_r^s(E_2, E_0) = g_s E_1 E_2 S_s^r(E_1 E_2) \left[\frac{4 \cdot 2m}{2(2\pi)^2 \hbar^3} \right]$$

Simplifying the arithmetical bracket and utilizing energy conservation in the forms

$$E_0 - I_r = E_1 + E_2 + I_s \ ,$$

or

$$E_0 = E_1 + E_2 + \zeta_0 \qquad (\zeta_0 = I_r - I_s) \ ,$$

we finally achieve Fowler's result [his Eq (C)]

$$g_r E_0 S_r^s(E_2, E_1 + E_2 + \zeta_0) = g_s E_1 E_2 S_s^r(E_1, E_2) \left(\frac{8\pi m}{h^3} \right)$$

With the connection between the ionization cross section,
$\sigma_{e\text{-ion}}(rE_0 \to sE_1E_2)dE_2$ and the recombination rate, our analysis of
detailed balancing is essentially complete. Before deducing the
recombination rate from our rather limited knowledge of ionization
cross sections, we note that the general form of the energy dependence
of the recombination rate is

$$W_{3\text{-rec}}(E_1E_2s \to E_0r) \quad \propto \quad \frac{E_0}{\sqrt{E_1E_2}} \; \sigma_{e\text{-ion}}(E_0r \to E_1E_2s) \; .$$

Let us now consider the limit, $E_1, E_2 \to 0$, which, for the inverse
process, corresponds to approaching the threshold, since
$E_0 = (E_1 + E_2) + C_0$. One can show that this particular ionization
cross section remains finite at threshold but that the integrated
ionization cross section vanishes. We, therefore, have

$$W_{3\text{-rec}}(E_1E_2s \to E_0r) \quad \underset{E_1, E_2 \to 0}{\propto} \quad \frac{\text{Constant}}{\sqrt{E_1E_2}}$$

One last general result is the recording of the rates of change of
population of the rth atomic level by recombination from the sth ionic
level and by the inverse ionization process. Integrating our previous
rate over all electron energies gives

$$\left(\frac{dn_r}{dt}\right)_{3\text{-rec}} = \frac{2}{\hbar}\left[\frac{(2\pi)^2}{\left(\frac{2m}{\hbar^2}\right)^2}\right]\frac{g_r}{g_s} \; n_s \int_0^\infty dE_1 \int_0^\infty dE_2 \, g(E_1)g(E_2)\frac{E_0}{\sqrt{E_1E_2}} \; \sigma_{e\text{-ion}}(E_0r \to E_1E_2s) \; ,$$

where, of course, $E_0 = E_1 + E_2 + C_0$ $(C_0 = I_r - I_s)$. The loss due to
ionization is

$$\left(\frac{dn_r}{dt}\right)_{e\text{-ion}} = -n_r \int_0^\infty dE_2 \int_{C_0 + E_2}^\infty dE_0 \, g(E_0)\sqrt{\frac{2E_0}{m}} \; \sigma_{e\text{-ion}}(E_0r \to E_0 - E_2 - C_0, E_2s)$$

If the electrons have a Maxwellian distribution, these rates become

$$\left(\frac{dn_r}{dt}\right)_{3\text{-rec}} = \frac{32\pi}{\hbar\left(\frac{2m}{\hbar^2}\right)^2} \frac{g_r}{g_s} n_e^2 n_s \frac{1}{(kT)^3} \frac{1}{2} \int_0^\infty dE_1 \int_0^\infty dE_2 \; E_o e^{-\frac{E_1+E_2}{kT}} \sigma_{e\text{-ion}}(E_o r \to E_1 E_2 s)$$

and

$$\left(\frac{dn_r}{dt}\right)_{e\text{-ion}} = -\sqrt{\frac{8}{m\pi(kT)^3}} \; n_e n_r \int_0^\infty dE_2 \int_{\zeta_o+E_2}^\infty dE_o \; E_o e^{-\frac{E_o}{kT}} \sigma_{e\text{-ion}}(E_o r \to E_1 E_2 s)$$

where a factor of 1/2 has been inserted in the first expression to take into account the identity of the electrons. If we further assume the existence of complete thermal equilibrium for the atoms and ions as well as electrons, and consider these processes as the only ones occurring, then we can investigate the result of setting

$$\frac{dn_r}{dt} = \left(\frac{dn_r}{dt}\right)_{3\text{-rec}} + \left(\frac{dn_r}{dt}\right)_{e\text{-ion}} = 0 \quad \text{(for equilibrium)}$$

Replacing the variable E_o by E_1 in the second term (see integration region) we obtain the condition
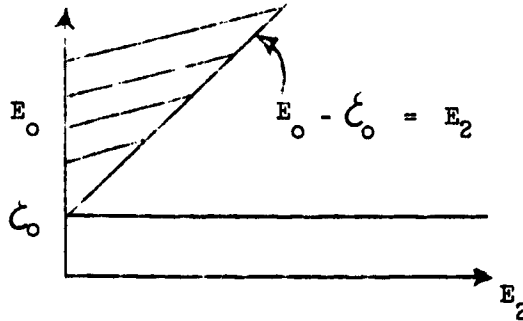
$$0 = -\frac{1}{2} \int_0^\infty dE_1 \int_0^\infty dE_2 \; e^{-\frac{E_1+E_2}{kT}} E_o \sigma_{e\text{-ion}}(E_o r \to E_1 E_2 s) n_e \sqrt{\frac{8}{m\pi(kT)^3}}$$

$$\times \left\{ n_r e^{-\frac{E_o}{kT}} - \frac{g_r}{g_s} n_e n_s \frac{2^{3/2}\hbar^3\pi^{3/2}}{m^{3/2}(kT)^{3/2}} \right\}$$

Setting the face bracket to zero and introducing the thermal deBroglie wave length

$$\lambda = \sqrt{\frac{h^2}{2\pi mkT}} \,,$$

we obtain the so-called <u>Saha</u> <u>relation</u> between the populations of the atomic and ionic levels and the electron density

$$\frac{n_e n_s}{n_r} = \frac{1}{\lambda^3} \frac{g_s}{g_r} e^{-\frac{I_s - I_r}{kT}} \,.$$

In general, this equation follows directly from the application of the Boltzmann distribution to an <u>ideal</u> ionized gas, the factor λ^3 arising, of course, from the continuum nature of the electron states. In terms of total numbers, the Saha equation is

$$\frac{N_e N_s}{N_r} = \frac{V}{\lambda^3} \frac{g_s e^{I_s/kT}}{g_r e^{I_r/kT}} \,.$$

Fowler's detailed balancing result discussed above followed, of course, from this relation as the starting point.

C. Thomson's Theory of Ionization and Three-Body Recombination

In 1912, Thomson formulated a classical theory for the ionization of an atom by an incident charged particle. In modern terms, his theory was the first "knock-out" or "direct-interaction" model for particle disintegration processes. According to Thomson, the incident particle makes a Coulomb collision with a target electron. If the energy transferred to the struck electron is greater than its binding energy, then the atom is ionized; otherwise, it is simply excited.

We can easily obtain Thomson's result, which is valid if the incident velocity is much greater than the velocities of the target electrons; in other words, if the target electrons can be considered as stationary. We need to recall only two simple facts from scattering theory. First of all, if we are dealing with two particles of equal mass, then the energy Q transferred to the struck particle is

$$Q = T \sin^2 \frac{\theta}{2} ,$$

when θ is the center of mass scattering angle and T is the incident kinetic energy (Q and T are laboratory-system energies). Second, the center of mass scattering angle for the classical Coulomb scattering of two electrons is determined by the relation

$$\cot \frac{\theta}{2} = \frac{s}{d} \qquad\qquad d = \frac{e^2}{T} .$$

Using the fact that $\sin^2 \frac{\theta}{2} = [1 + \cot^2 \frac{\theta}{2}]^{-1}$, the energy loss or transferred energy can then be written as a function of T and s:

$$Q(s,T) = T \frac{1}{1 + (s/d)^2} ,$$

or

$$\sigma(T,Q)dQ = \pi d^2 \frac{T dQ}{Q^2}$$

This is the basic formula in Thomson's classical theory of energy loss-- with particular reference to ionization--or in slightly different form

$$\sigma(T,Q)dQ = \pi e^4 \frac{1}{T} \frac{dQ}{Q^2} .$$

We shall adapt this formula to the particular case of the target being in the rth level of the H-atom. Energy conservation in our previous notation is

$$E_o - I_r = E_1 + E_2 \ ,$$

where $T = E_o$ and

$$Q = E_o - E_1 = E_2 + I_r$$

so that $dQ = dE_2$. Thus, the cross section previously introduced is

$$\sigma_{e\text{-ion}}(E_o r \to E_1 E_2)dE_2 = \pi e^4 \frac{1}{E_o} \frac{1}{(E_2 + I_r)^2} \ dE_2 \quad (E_2 > 0)$$

Measuring energies in terms of the ionization potential and lengths in terms of the first Bohr radius, we find that

$$\sigma_{e\text{-ion}}(E_o r \to E_1 E_2) = \pi e^4 \frac{1}{E_o(E_2 + I_r)^2}$$

$$= 4\pi a_o^2 \left(\frac{R}{I_r}\right)^2 \frac{1}{u_o(u_2 + 1)^2} \ \frac{1}{I_r}$$

or

$$\sigma_{e\text{-ion}}(E_o r \to E_1 E_2) = 4\pi (r^2 a_o)^2 \frac{1}{u_o(u_2 + 1)^2} \left(\frac{1}{I_r}\right)$$

Although this is the cross section we need, one often encounters the total ionization cross section

$$\sigma_{ion}(E_o r) = \int_{I_r}^{T} dQ \ \sigma_e(E_o r \to E_1 E_2) = \int_{o}^{T} dE_2 \ \sigma_{e\text{-ion}}(E_o r \to E_1 E_2)$$

$$= 4\pi (r^2 a_o)^2 \frac{1}{u_o} \int_{o}^{u_o-1} du \ \frac{1}{(u + 1)^2}$$

$$\sigma_{ion}(E_o r) = 4\pi (r^2 a_o)^2 \frac{1}{u_o} \left(1 - \frac{1}{u_o}\right) \quad .$$

For very high incident energies ($u_o \gg 1$), where one might expect these formulae to be most appropriate, it becomes

$$\sigma_{ion}(E_o r) \xrightarrow[E_o \gg I_r]{} 4\pi(r^2 a_o)^2 \frac{1}{u_o} = 4\pi(r a_o)^2 \frac{1}{E_o/R} \quad .$$

We observe that it differs from the geometric area of the classical Bohr orbit by the factor $\frac{1}{u_o} = \frac{1}{r^2}(\frac{R}{E_o})$. The threshold behavior is

$$\sigma_{ion}(E_o r) \xrightarrow[u_o \to 1]{} 4\pi(r^2 a_o)^2 (u_o - 1) \, ,$$

which is apparently in conformity with the quantum mechanical prediction regarding the dependence on energy. Likewise, the cross section of interest in recombination seems to have the right threshold behavior

$$\sigma_{e-ion}(E_o r \to E_1 E_2) \xrightarrow[\substack{u_o \to 1 \\ u_2 \to 0}]{} 4\pi(r^2 a_o)^2 \frac{1}{I_r} = 4\pi a_o^2 \left(\frac{r^2}{R} \right)$$

On the other hand, the classical theory disagrees with experiments near threshold by being at least a factor of four too large, and at very high energies where quantum mechanical calculations imply an $E_o^{-1} \log E_o$ energy dependence.

All of these formulae are based on assuming the target electron's velocity to be small compared with the incident velocity. The effect of the target electron's velocity was studied by L. H. Thomas [D2], who obtained the result

$$\sigma_{Thomas} = \sigma_{Thomson} \left[1 + \frac{4}{3} \frac{1}{u_2 + 1} \right] \quad .$$

More recent studies of classical scattering theory by Gryzinski [D3,4] include additional corrections. These are based on an approximation which, though certainly valid for high incident energy, breaks down as $E_o \to E_1$. For purposes of simplicity, we will usually not include these corrections in the following discussion and use the simple Thomson formula. In this connection, it may be noted that the Thomson formula does, in fact, follow/the Born approximation in the limit $E_o \gg Q \gg I_r$.
from

The form of the Thomas correction also follows from the plane-wave
Born approximation, but not the numerical factor 4/3.

Let us now examine the ionization and recombination rates of change of
the population of the rth hydrogenic level using just the Thomson cross section
and assuming thermal equilibrium for the electron distribution. Combining
the results of the previous section with this one leads to the formulae

$$\left(\frac{dn_r}{dt}\right)_{e-ion} = - n_e n_r \left\{ 4\lambda(r^2 a_0)^2 \left(\frac{I_r}{\hbar}\right)\left(\frac{I_r}{kT_e}\right) E_2 \left(\frac{I_r}{kT_e}\right)\right\}$$

$$\left(\frac{dn_r}{dt}\right)_{3-rec} = + n_e^2 n_i \left\{ 4\lambda(r^2 a_0^2)^2 \lambda^3 \left(\frac{kT_e}{\hbar}\right) r^2 G_2 \left(\frac{I_r}{kT_e}\right)\right\}$$

where

$$E_n(x) = \int_x^\infty dt \, \frac{e^{-t}}{t^n} \quad \text{and} \quad G_n(x) = x^n e^x E_2(x) \quad.$$

The function $G_n(x)$ has the special properties $G_2(0) = 0$, $G_n(\infty) = 1$, and
$G_n'(x) > 0$. In complete thermal equilibrium, these rates are equal in
conformity with the Saha relation. These equations have been written in
such a way that the dimensions can be easily checked, of course recalling
in this connection that λ is the thermal deBroglie wave length and that
$I_r/\hbar$ and $kT/\hbar$ have the dimensions of one over time. We have also preserved
the characteristic classical area $(r^2 a_0)^2$ associated with level r. If we
use the Thomas correction, then we have to make the replacements

$$E_2(x) \rightarrow E_2(x) + \frac{4}{3} x E_3(x)$$

and

$$G_2(x) \rightarrow G_2(x) + \frac{4}{3} G_3(x) \quad.$$

By analogy with the radiative recombination, we can define a three-body
recombination coefficient β_r such that

$$\left(\frac{dn_r}{dt}\right)_{3-rec} = \beta_r n_e n_i \quad, \qquad\qquad \frac{cm^3}{sec}$$

where β_r must, of course, be proportional to the electron density

$$\beta_r = 4r^2(\lambda^3 n_e)\, \lambda(r^2 a_o)^2\, \frac{kT_e}{\hbar}\, G_2\left(\frac{I_r}{kT_e}\right)$$

For any given level, we can define high and low temperature limits, and use the special forms of G_2 in these limits to obtain

$$\beta_r \rightarrow 4r^2(\lambda^3 n_e)\, \lambda(r^2 a_o)^2\, \frac{kT_e}{\hbar}
\begin{cases}
1 & kT_e \ll I_r \\[2ex]
\frac{1}{2}\left(\frac{I_r}{kT_e}\right) & kT_e \gg I_r
\end{cases}$$

In the low temperature limit, $\beta_r \propto 1/T$, whereas in the high-temperature limit, it varies as $1/T^2$. The low-temperature limit has the numerical form

$$\beta_r \rightarrow 5r^6 \times 10^{-31}\, \frac{cm^6}{sec}\, \frac{n_e}{T'_e}\ ,$$

where T'_e is the temperature in electron volts. If we include the Thomas factor in the ionization cross section, this gives a correction factor

$$1 + \frac{4}{3}\, \frac{G_3(x)}{G_2(x)} = 1 + \frac{4}{3} \times \frac{E_3(x)}{E_2(x)}\ ,$$

which, for $x \rightarrow \infty$, obviously approaches $1 + 4/3 + O(1/x)$ and, therefore, gives a large correction and, for $x \rightarrow 0$, approaches unity. Neither of these modifications changes the quoted asymptotic temperature dependence, although the detailed form of the cross section at low energies is obviously important.

The above recombination and ionization rates were first explicitly written and applied by Giovanelli in 1948 [C3] using, of course, Thomson's original results. In order to make some improvement in the Thomson cross section, Giovanelli multiplied it by a factor of two, which should be compared with the Thomas modification at low temperatures and gives the simple factor $2\frac{1}{3}$.

To get an idea of the magnitude of β_r, we might consider the ratio of radiative to three-body recombination coefficients in the low-temperature limit

$$\frac{\beta_r}{\alpha_r} \xrightarrow[kT \ll I_r]{} \frac{9r^6 \times 10^{-31}\, \frac{cm^6}{sec}\, \frac{n_e}{T'}}{\left(2 \times 10^7\, \frac{cm}{sec}\right)\left(10^{-22}\, cm^2\right) 2r \left(\frac{I_r}{kT_e}\right)\sqrt{\frac{T'}{.1}}}$$

$$\approx \left[\frac{r^7}{\sqrt{T'}}\quad \frac{n_e}{6 \times 10^{16}/cm^3}\right]$$

At a temperature corresponding to $T' = 1$ volt, we see that $\beta_1 = \alpha$ for a density of $6 \times 10^{16}/cm^3$. On the other hand, the seventh power of r is very effective, so that for high states, three-body recombination will become important at much lower densities; lower temperatures also have the same, but not as strong, effect. For example, at 300°, $\beta_{10} = \alpha_{10}$ at the rather low density of $10^9/cm^3$; however, the higher excited states will be more easily destroyed by ionization processes, so that the three-body recombination is important for large, but not arbitrarily large, principal quantum numbers.

IV - Qualitative Discussion of "Collisional-Radiative" Recombination

We have so far given an introduction to some of the atomic processes important in recombination, particularly the radiative and three-body recombination reactions and their inverses. To study the actual time development of the populations, one must include these as loss and gain mechanisms--plus others, such as spontaneous decay, elastic collisions, inelastic and superelastic collisions. As has been emphasized, our information on most of these processes, with the exception of the radiative ones, is quite meager, and heavy reliance is now being placed on classical collision theory. The solution of the rate equations for any particular problem is quite difficult in that it essentially involves an infinite set of coupled equations containing many unknown reaction rates.

As far as laboratory experiments are concerned, the first interpretations involved purely radiative processes. Unfortunately, the measured decay rates were consistently larger by two orders of magnitude than the radiative recombination coefficients given above. It was only two years ago that D'Angelo suggested that three-body recombination might be responsible for the discrepancy [C4]. This idea had actually been in circulation for some time and three-body recombination has, of course, been considered in various astrophysical applications. (According to Dr. W. Kunkel, the large recombination coefficients found in early experiments are suspect because of the important effects of diffusion to the walls.) D'Angelo considered the following processes to occur: (a) radiative recombination, (b) three-body recombination, (c) ionization by electron impact, and (d) spontaneous decay. He argued that, at sufficiently high plasma density, the dominant recombination process is three-body recombination to states of "intermediate" principal quantum numbers which then decay radiatively. States with very high principal quantum numbers are immediately reionized, i.e., are in so-called "Saha equilibrium", whereas states with very low principal quantum numbers are directly populated via the radiative recombination process. Of course, the meaning of large and small principal quantum numbers depends on the pressure and temperature. For example, D'Angelo found that the recombination at $T = 3000°K$ has its maximum contribution from $r = 6$ and 7 in the density range from 10^{12} to $10^{13}/cm^3$, which is the density range where the recombination coefficient has just become proportional to density according to his calculations.

It was soon pointed out by Bates, Kingston, and McWhirter that D'Angelo's neglect of inelastic and superelastic collisions was actually more important than supposed [C6]. In particular, collisional de-excitation of excited atoms formed by three-body recombination was very effective in preserving these neutral species. In fact, the decay of the excited states seems to be the controlling process at intermediate densities, as has been emphasized by Byron, Stabler, and Bortz [C7].

Without going into details of the calculations of Bates and coworkers, we can present the following simplified picture of the recombination process for hydrogenic plasmas which are transparent to radiation and which have temperatures less than the excitation energy of the first excited state of the hydrogen atom: The levels with very large principal quantum numbers are in thermal equilibrium at the electron temperature, i.e., in "Saha equilibrium." This equilibrium is achieved by the very rapid three-body recombination and the inverse ionization, aided in an essential way by elastic collisions and particularly de-excitation processes. This last mechanism implies that there are levels with intermediate values of the principal quantum number which are not populated appreciably by direct recombination, but by decay from higher states. The total recombination rate is then determined by the rate at which the population of these near-equilibrium states can decay by de-excitation to lower states. Now this de-excitation is made up of two parts: <u>radiative</u> decay which <u>decreases</u> rapidly with n and <u>collisional</u> decay which <u>increases</u> rapidly with n, hence giving a maximum at some intermediate value of r, say r_m, which depends on the density. Byron et al have, in fact, been able to reproduce the work of Bates by simply setting the recombination coefficient equal to the de-excitation rate of the level r_m, the level with the largest rate. For $r > r_m$ (roughly speaking), we have Saha equilibrium, which provides a kind of reservoir of recombined excited atoms. The fact that the decay of excited states plays such a dominant role has the effect of masking the importance of three-body recombination. For example, the transition region from radiative to three-body recombination can occur over a very wide range of density, e.g., from 10^9 to 10^{17} at $T = 16,000°$ K.

These last paragraphs are meant only as a guide to the present physical picture of the recombination process in moderately dense hydrogenic plasmas. The phenomena are obviously very complex and are not only difficult to treat

theoretically but are elusive to quantitative measurement. Recent
spectroscopic studies have proved very valuable [C5], but it is clear
that there is room for many new techniques in this field. The great
popularity of classical collision theory for treating the three-body
recombination process and superelastic collisions also indicates the
desparate need for improvements in the theory of atomic collisions.

References

A. General Reviews

1. Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Ch. VI, Sec. 2 and Ch. X (Oxford, 1952).

2. G. Elwert, Zs. Naturforschung, 7a, 432 (1952).

3. Bates and Dalgarno, *Atomic and Molecular Processes*, Ch VII (Academic, 1962).

4. D. H. Menzel, *Selected Papers on Physical Processes in Ionized Plasmas* (Dover, 1962).

B. Radiative Recombination

1. H. A. Kramers, Phil Mag 46, 836 (1923).

2. E. A. Milne, Phil Mag 47, 209 (1924).

3. M. J. Seaton, Mon Nat Roy Ast Soc 119, 81 and 90 (1959).

C. Three-Body Recombination

1. R. H. Fowler, Phil Mag 47, 257 (1924).

2. R. H. Fowler, *Statistical Mechanics*, Ch 17 (Cambridge, 1936).

3. R. G. Giovanelli, Australian J. Sci. A 1, 275 and 289 (1948).

4. N. D'Angelo, Phys Rev 121, 505 (1961).

5. E. Hinnov and J. G. Hirschberg, Phys Rev 125, 795 (1962).

6. D. R. Bates, A. E. Kingston, R. W. P. McWhirter, Proc Roy Soc A267, 297 (1962) and A270, 1155 (1962).

7. S. Byron, R. C. Stabler, P. I. Bortz, Phys Rev Letters 8, 376 (1962).

D. *Collisions of Electrons with Atoms*

1. J. J. Thomson, Phil Mag 23, 449 (1912).

2. L. H. Thomas, Proc Camb Phil Soc 23, 829 (1927).

3. M. Gryzinski, Phys Rev 107, 1471 (1957) and Phys Rev 115, 374 (1959).